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## **Low-temperature synthesis under low oxygen pressure and thermodynamic properties of $\text{YbFe}_2\text{O}_{4-\delta}$**

The mixed-valence compound  $\text{YbFe}_2\text{O}_{4-\delta}$  was synthesized using a modified method that allows employing gaseous atmosphere with a controlled ratio of inert gas and oxygen. The stability range for  $\text{YbFe}_2\text{O}_{4-\delta}$  was determined at 1090 °C under reducing conditions. Thermodynamic characteristics for the formation of  $\text{YbFe}_2\text{O}_{4-\delta}$  from the simple oxides and from elements in the temperature range 700–910 °C have been calculated. The obtained results allow specifying the low-temperature part of P-T-X diagram for the Yb-Fe-O system.

**Keywords:** oxygen partial pressure, mixed-valence compound, thermodynamic properties, complex oxides, oxygen nonstoichiometry

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### **Introduction**

Complex oxides  $\text{RFe}_2\text{O}_4$  ( $\text{R} = \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$ ), which demonstrate both ferroelectric and ferromagnetic properties, are presenting a special class of materials called multiferroics. These materials are promising for application in energy-saving and storage devices [1]. The information concerning physicochemical properties for these complex oxides is important for their synthesis and practical applications. One of the representatives of such materials is  $\text{YbFe}_2\text{O}_4$ .

Taking into account that  $\text{YbFe}_2\text{O}_4$  contains iron in two oxidation states,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , it is obvious that one of the important parameters for its synthesis is oxygen partial pressure in gaseous phase. Since the compound is stable only within narrow interval of temperature and oxygen partial pressure [2, 3], it is very important to es-

tablish a synthesis protocol and to find the temperature and oxygen partial pressure ranges of its stability. Based on the ionic radii of rare earth ions  $\text{R}^{3+}$  [2], the whole set of R-Fe-O systems can be divided into four groups. The Yb-Fe-O system belongs to the forth group D, in which  $\text{R}_2\text{Fe}_3\text{O}_7$  exists together with  $\text{RFeO}_3$ ,  $\text{R}_3\text{Fe}_5\text{O}_{12}$  and  $\text{RFe}_2\text{O}_4$ . The decrease of temperature may cause a decomposition of  $\text{R}_2\text{Fe}_3\text{O}_7$  and, as a result, the Yb-Fe-O system would be converted to the group C [4]. The synthesis of mixed-valence compounds in the R-Fe-O systems belonging to the C and D groups is traditionally performed under low oxygen partial pressure employing  $\text{H}_2$  and  $\text{CO}_2$  mixtures [2–4]. In works [2–4] raw mixtures of  $\text{R}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were annealed at temperature 1200 °C in flow of gas with low oxygen activity. A precise

control and maintenance of oxygen partial pressure in such gaseous mixtures in contact with oxide sample is not an easy task. The information about the possibility of  $\text{YbFe}_2\text{O}_4$  synthesis at temperatures lower than 1200 °C is absent. The purpose

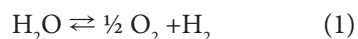
of the present study is the determination of conditions for preparation of  $\text{YbFe}_2\text{O}_4$  at temperatures lower than 1200 °C, and investigation of its physicochemical properties in the low-temperature range.

## Experimental

$\text{YbFe}_2\text{O}_{4-6}$  was synthesized by the advanced method in which gas mixture of argon and oxygen was used. Reducing conditions were provided by maintaining the required value of oxygen partial pressure using the electrochemical method [5]. An interaction of a sample with the gaseous  $\text{Ar-O}_2$  mixture can only result in oxygen exchange, while using of  $\text{CO}_2\text{-H}_2$  mixture may lead to the formation of carbides.

Preliminarily dried powders of  $\text{Fe}_2\text{O}_3$  (purity  $\geq 98\%$ ) and  $\text{Yb}_2\text{O}_3$  (purity 99,9%) were mixed in equimolar amounts and grinded in an agate mortar for an hour, and then pressed into pellets with the diameter of 10 mm. The heat treatment was performed inside the airtight apparatus with a confined internal space (Fig. 1). A sample in a crucible 1 was placed in the quartz reactor 2 mounted in the furnace 3. Air was evacuated by the vacuum pump 4 out of the apparatus which was followed by refilling with argon. Oxygen partial pressure in the gas phase inside the apparatus was maintained and controlled by the oxygen cell 5, which consists of the oxygen sensor 6 and the oxygen pump 7. The oxygen cell was operated by the programmable oxygen pressure controller 8. Since the thermal condition for each sample synthesis was tuned individually, but the oxygen cell worked at the limited temperature range 600–900 °C (the optimal temperature is about 800 °C) two temperature zones in the apparatus were created: one for the oxygen cell (furnace 9)

and another for samples (furnace 3), retaining a common gas space. Syntheses of  $\text{YbFe}_2\text{O}_{4-6}$  were carried out at 1090 °C for 48 hours. It should be noted that it is the highest possible temperature that can be used in this apparatus because quartz was used as the reactor material. The value of oxygen partial pressure in the furnace 9 was set in the interval  $p\text{O}_2 = 10^{-11.04}\text{--}10^{-12.84}$  atm. It's worth to note that in the region of low oxygen pressures  $p\text{O}_2$  is defined by the equilibrium constant of reaction (1) and also depends on temperature [6]:



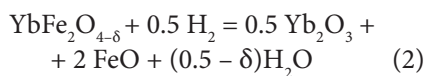
Due to this fact the oxygen pressure in the furnace 3 differed from  $p\text{O}_2$  which was achieved and measured in the furnace 6. The syntheses of samples in the furnace 3 at 1090 °C were performed in the interval  $p\text{O}_2 = 10^{-11.04}\text{--}10^{-12.84}$  atm. The circulation pump 10 was utilized to distribute the gas mixture with a controlled oxygen pressure evenly inside the apparatus. Manometer-vacuummeter 11 was used to measure the total gas pressure. The samples were quenched by pulling them out of the high temperature zone of the reactor into the space cooled by the flow of cold water.

The phase composition of quenched samples was determined by X-Ray diffraction (XRD) using a Shimadzu XRD7000C diffractometer (Cu K $\alpha$  radiation) in the range of angles  $20^\circ < 2\theta < 80^\circ$  with a step of  $0.2^\circ$ . The primary processing of diffraction data was performed with the software



Thus, it was experimentally determined that in the Yb–Fe–O system at 1090 °C  $\text{YbFe}_2\text{O}_{4-\delta}$  exists within the range of oxygen pressures  $p\text{O}_2 = 10^{-11.04} - 10^{-12.84}$  atm. This result significantly widens the temperature range for  $\text{YbFe}_2\text{O}_{4-\delta}$  stability, as compared to previous studies [2].

The absolute values of oxygen nonstoichiometry for samples prepared at various oxygen partial pressures were determined by means of gravimetric analysis via the hydrogen reduction of the samples to the stable simple oxides in the vacuum circulation setup as follows:



The absolute value of oxygen nonstoichiometry was calculated using equation (3):

$$\delta = \frac{M}{15.9994} - \frac{m \cdot M_{\text{red}}}{m_{\text{red}} \cdot 15.9994}, \quad (3)$$

where  $M$  is the molecular weight of the studied oxide,  $M_{\text{red}}$  is the total molecular

weight of solid products in the reduction reaction with allowance for the stoichiometric coefficients, 15.9994 is the atomic weight of oxygen,  $m_{\text{red}}$  is the weight of solid products after reduction reaction at the temperature of the experiment and  $m$  is the sample weight. Detailed description of the procedure is given in [7]. A decrease of the oxygen partial pressure during synthesis results in formation of oxygen vacancies and consequent change of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio. At the same time the unit cell parameter  $a$  increases while the oxygen partial pressure is reduced (Fig. 4, Table 1).

The obtained relationship between oxygen nonstoichiometry  $\delta$ , which is influenced by oxygen partial pressure and the unit cell parameter  $a$  (Fig. 5), might be used as a criterion for oxygen nonstoichiometry  $\delta$  estimation using only XRD results.

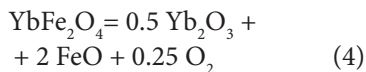
The measurements of  $\text{YbFe}_2\text{O}_{4-\delta}$  thermodynamic stability have been carried out using the vacuum circulation apparatus by static method [7] in the temperature range 700–910 °C. The high temperature

Conditions of  $\text{YbFe}_2\text{O}_{4-\delta}$  synthesis

Sample	$\lg(p\text{O}_2)$ (atm) at 1090 °C	Unit cell parameter $a, c$ (Å)	Oxygen nonstoichiometry $\delta$
1	–11.4	$a = 3.4506(4)$ $c = 25.0773(19)$ $V = 258.576$	0.033
2	–11.6	$a = 3.4519(4)$ $c = 25.0655(20)$ $V = 258.656$	0.038
3	–11.8	$a = 3.4528(4)$ $c = 25.0865(20)$ $V = 259.011$	0.041
4	–12	$a = 3.4538(4)$ $c = 25.0855(21)$ $V = 259.157$	0.048
5	–12.2	$a = 3.4547(4)$ $c = 25.0715(20)$ $V = 259.133$	0.061

Table 1

dissociation process of  $\text{YbFe}_2\text{O}_4$  at low oxygen partial pressure within the range  $p\text{O}_2 = 10^{-16.4} - 10^{-20.8}$  atm as a first approximation was written neglecting oxygen nonstoichiometry of ytterbium ferrite and oxygen nonstoichiometry of simple iron oxide as follows:



A linear function was fitted to the measured values of equilibrium oxygen partial pressure of the reaction (4) vs temperature (filled point in Fig. 6), and the following equation was obtained:

$$\lg(p\text{O}_2, \text{Pa}) = 11.78 - 27350/T \pm 0.04 \quad (5)$$

Unfilled point 2 (Fig. 6) corresponds to the equilibrium oxygen partial pressure

measured at 1200 °C by Kimizuka et al. [3]. One can observe good agreement of our results with those obtained earlier. Finally, Eq. (5) was recalculated to the standard Gibbs energy for reaction (4):

$$\Delta G_T^0 = 130.895 - 0.0564T \pm 0.99 \text{ kJ/mol} \quad (6)$$

Since the coefficients in Eq. (6) can be treated as  $\Delta H_T^0$  and  $\Delta S_T^0$ , respectively, for reaction (4), the changes of standard entropy and enthalpy for  $\text{YbFe}_2\text{O}_4$  formation from elements can be calculated taken into account the values of the thermodynamic functions for the simple oxides' ( $\text{Yb}_2\text{O}_3$  and  $\text{FeO}$ ) formation [9,10]:  $\Delta H_f^0(\text{YbFe}_2\text{O}_4) = -1575.767 \text{ kJ/mol}$ ,  $\Delta S_f^0 = 274.23 \text{ kJ/mol/K}$ .

## Conclusions

It was found that  $\text{YbFe}_2\text{O}_4$  can be prepared at 1090 °C within the oxygen partial pressure range  $p\text{O}_2 = 10^{-11.04} - 10^{-12.84}$  atm. The obtained results allow specifying the low-temperature part of P-T-X diagram for the Yb-Fe-O system, which is very important from the practical point of view since it allows choosing the conditions for  $\text{YbFe}_2\text{O}_4$  synthesis and usage. Using the static method in the vacuum circula-

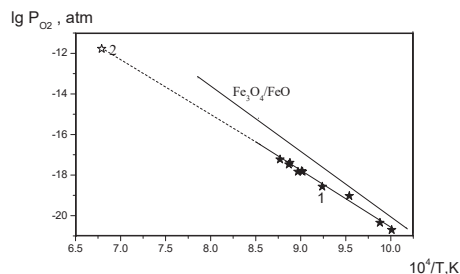


Fig. 6. Equilibrium oxygen partial pressure of  $\text{YbFe}_2\text{O}_4$  dissociation (reaction 4) versus reciprocal temperature: 1 – our data, 2 – reported in [3]

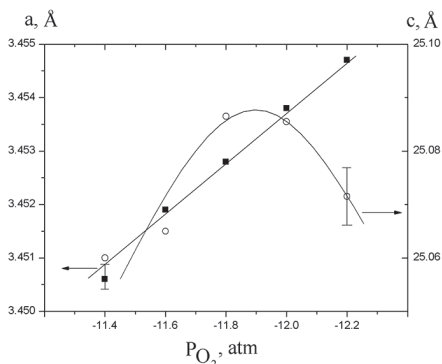


Fig. 4. Dependence of the unit cell parameter  $a$  and  $c$  on oxygen partial pressure for  $\text{YbFe}_{2\pm\delta}\text{O}_{4\pm\delta}$  synthesis

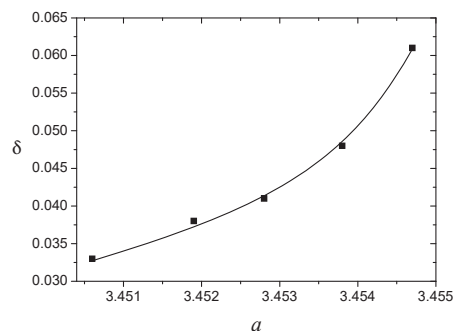


Fig. 5. Dependence of oxygen nonstoichiometry on unit cell parameter  $a$  for  $\text{YbFe}_{2\pm\delta}\text{O}_{4\pm\delta}$

tion apparatus, the decomposition oxygen partial pressure was measured. Finally, the changes of standard entropy and enthalpy

of  $\text{YbFe}_2\text{O}_4$  formation from elements in the temperature range 700–910 °C were calculated.

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